

Detection of Hydrated Silicates in Crustal Outcrops in the Northern Plains of Mars

J. Carter,^{1*} F. Poulet,¹ J.-P. Bibring,¹ S. Murchie²

The composition of the ancient martian crust is a key ingredient in deciphering the environment and evolution of early Mars. We present an analysis of the composition of large craters in the martian northern plains based on data from spaceborne imaging spectrometers. Nine of the craters have excavated assemblages of phyllosilicates from ancient, Noachian crust buried beneath the plains' cover. The phyllosilicates are indistinguishable from those exposed in widespread locations in the southern highlands, demonstrating that liquid water once altered both hemispheres of Mars.

Data acquired by the OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité) (1) and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) (2) instruments on board Mars Express and Mars Reconnaissance Orbiter, respectively, have confirmed that the surface of the ancient, Noachian-aged southern highlands is mostly unaltered, preserving old crustal materials (3–5), and revealed thousands of small outcrops of various hydrated silicates, mostly phyllosilicates (6–8). These altered minerals record an early era during which Mars likely harbored environmental conditions that sustained surface and subsurface liquid water. By contrast, in the younger northern lowlands that cover one-third of the planet, a hundreds-of-meters-to-few-kilometers-

thick cover, interpreted to be volcanic and detrital sediments partly reworked by glacial processes, buries preexisting crust thought to be analogous to that in the southern highlands (9, 10). Contrary to the highlands, the surface has a large dust cover index (11) and displays only weak and localized signatures of olivine and pyroxene, with no hydrated silicates (4, 12–14). The structure and composition of the underlying crust are nearly unknown in spite of attempts to constrain them by surface altimetry and subsurface radar sounding (15, 16).

An efficient way to access the crust buried beneath the northern plains is to study material ejected by impactors large enough to create craters tens of kilometers in diameter and penetrate to several kilometers in depth (17), below the Hesperian cover: Although violent, the cratering process partly preserves the composition of the ejected material. Previous studies of craters within the northern plains have included a thorough survey of their morphology (10, 18) and of their spectral signatures, revealing that olivine

is ubiquitous in craters larger than tens of km (13, 19, 20). After tentative detections of phyllosilicates in a few northern plains craters by OMEGA (fig. S1) (21), we used surface reflectance data from CRISM to investigate the composition of northern plains craters, focusing on central peaks, rims, and ejecta. CRISM acquires spectra of the surface covering 0.4 to 3.9 μm at a spatial sampling of 18 m per pixel, spectrally sampled at 6.5 nm (2).

We analyzed all craters greater than 30 km for which CRISM data were available and dozens of craters with diameters ranging from 4 to 30 km. We excluded from our survey observations of sites covered by seasonal ice. The remaining 160 high-resolution CRISM images cover 91 craters. Nine of them exhibit spectral signatures of hydrated minerals: Lyot, Kunowsky, Stokes, Santa Fe, Bamberg, and four unnamed craters. All nine craters are found in relatively young [$<2.5 \times 10^9$ years ago (Ga)] plains (Fig. 1), range in diameter from 20 to 60 km (except for the 230-km Lyot crater), and have well-exposed inner crater walls and rims. Preservation state varies greatly from one crater to another: Some are well preserved (e.g., Stokes, Santa Fe, and Bamberg), but overall northern plains craters have been heavily mantled and resurfaced by volcanic, glacial, periglacial, and sedimentary processes (9, 10, 18, 22–24).

We built spectral parameter maps representing strengths of specific metal-OH vibration bands that allow discriminating between various hydrated minerals, which all exhibit a 1.9- μm feature (Fig. 2). A band near 2.2 μm indicated the presence of Al-rich phyllosilicates, whereas Fe-rich and Mg-rich (Fe/Mg-rich) phyllosilicates were identified on the basis of absorption bands from 2.28 to 2.35 μm (6, 25). Chlorites and prehnite both exhibited bands between 2.2 and 2.4 μm , with prehnite uniquely identified by sharp bands

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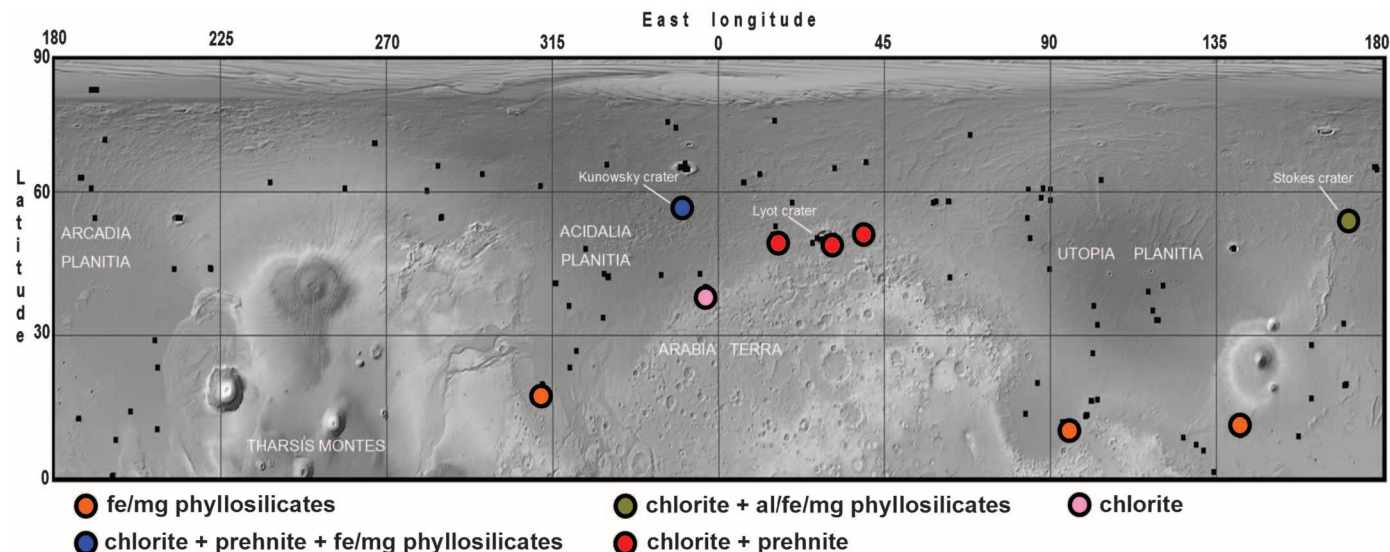


Fig. 1. Locations of nine exposures of hydrated silicate in northern plains craters, shown on a Mars Orbiter Laser Altimeter shaded relief map. Black squares indicate sites investigated with CRISM that did not yield detections.

at 2.35 and 1.48 μm . We also built maps of mafic mineral bands (resulting from olivine and pyroxene) based on absorptions in the 1- to 2.5- μm wavelength range (26).

By using these spectral criteria, we detected a variety of hydrated minerals. Signatures consistent with Fe/Mg phyllosilicates and chlorites were found in six out of nine sites, whereas Al-rich phyllosilicates were only found at Stokes crater (Fig. 2). At least four sites had signatures consistent with prehnite, and three sites may have contained a chlorite-prehnite assemblage, identifiable by their band shapes around 2.35 μm and the presence of two distinct shallow bands at 1.4 and 1.48 μm . Three lower-latitude craters had spectral signatures in their central mound consistent, at an 18-m-per-pixel scale, with either olivine partly altered into Fe/Mg-rich clay or subpixel mixtures of olivine and clay. In addition to hydrated minerals, all of the large craters had strong olivine signatures both in their bedrock and in dark dunes on the crater floors, in close proximity to the hydrated mineral deposits. Smaller pyroxene-bearing outcrops were also identified in the central peaks in a few craters.

All nine craters with hydrated minerals are located equatorward of 60°N (Fig. 1); six are close to the highlands units, and the remaining

three are at distances > 1000 km. The hydrated minerals occur in the craters' central peaks with the exception of the Lyot crater, for which the relevant signatures were observed in inner and outer rim materials. There is no consistent geological trend regarding association with preservation state: Some occurrences were in degraded outcrops or knobs, whereas others were associated with mobile material. A given hydrated mineral specie may be found in different settings within a crater, suggesting erosion and aeolian transport.

Stokes, a 60-km crater located in northern Arcadia Planitia, exemplifies the diversity in hydrated mineral composition and morphological setting (Fig. 3). It is a complex crater with a highly fractured central uplift. Its major features include knobs, scarps, km-scale outcrops, and evidence for aeolian erosion and sedimentation. No periglacial mantling processes are evident at the scale of High-Resolution Imaging Science Experiment (HiRISE) images (<50 cm per pixel).

We detected numerous hydrated silicate signatures at various locations within Stokes. The spectral signatures agree well with those of two different aluminum phyllosilicates, montmorillonite and kaolinite, as well as with chlorites and mixed-layered Fe/Mg phyllosilicates/chlorites. The most spatially extensive hydrated mineral

signature is consistent with the aluminum smectite montmorillonite, which occurs in small-scale, light-toned outcrops along a 2-km-long scarp. There is strong evidence for erosion and downhill transport of the altered outcropping material (Fig. 3C). We identified dozens of occurrences of Al phyllosilicate consistent with kaolinite, typically <100 m in size. These were correlated with rough material in outcrops or knobs, with some evidence of limited erosion and transport. The iron-magnesium phyllosilicate-bearing unit was also found in outcropping material, usually in close proximity to the Al-rich units (Fig. 3D). Olivine and pyroxene signatures were correlated with light-toned outcrops in the central structure (Fig. 3B) that appear randomly fractured. Olivine is the most common mineral detected, and pyroxene was seen in a few outcrops; both were more common than hydrated mineral-bearing outcrops. Hydrated mineral outcrops are more fractured and less well preserved than the olivine outcrops. A few olivine outcrops displayed a 2.3- μm band consistent with altered olivine or a subpixel spatial mixture of olivine and phyllosilicate.

Kunowsky crater (Fig. 4) exhibited signatures of Fe/Mg-rich phyllosilicates and what we interpret as a chlorite-prehnite assemblage. At the 6-m-per-pixel scale of CTX (Context Camera, also on Mars Renaissance Orbiter) images (Fig. 4B), there is evidence for aeolian and/or slope-driven displacement of the chlorite/prehnite-bearing material, emanating from a mound east of the central uplift. At the scale of HiRISE images (Fig. 4C), Fe/Mg-rich phyllosilicates appear broadly correlated with hundreds-of-meters-scale outcrops or mounds. The 230-km-diameter Lyot crater, formed during the Early Amazonian period, is the largest and deepest northern plains crater, with a partly preserved rim and ejecta (fig. S2). Although fluvial valley systems within Lyot crater were formed during Middle or Late Amazonian (27), we detected a chlorite-prehnite unit on the outer rim, indicating formation distinct from valley formation (fig. S2B).

Four scenarios could account for the formation of hydrated minerals in northern plains craters. First, parent minerals, likely mafic, were altered in situ by aqueous surface processes after having been exhumed by impact. The presence of the low-grade metamorphic mineral prehnite, which forms under specific conditions of <3 kbar, 200° to 350°C (28), argues against formation by this process. Moreover, no morphological evidence at the regional or crater scale points toward the existence of transient or standing bodies of liquid water on the surface. Second, phyllosilicate-bearing material was transported by wind from highlands and deposited since the time of crater formation. The correlation of phyllosilicate signatures with outcrops or rocky units and the absence of such signatures in crater floor dunes and elsewhere in the northern plains are strong evidences against this scenario. Third, hydrated minerals

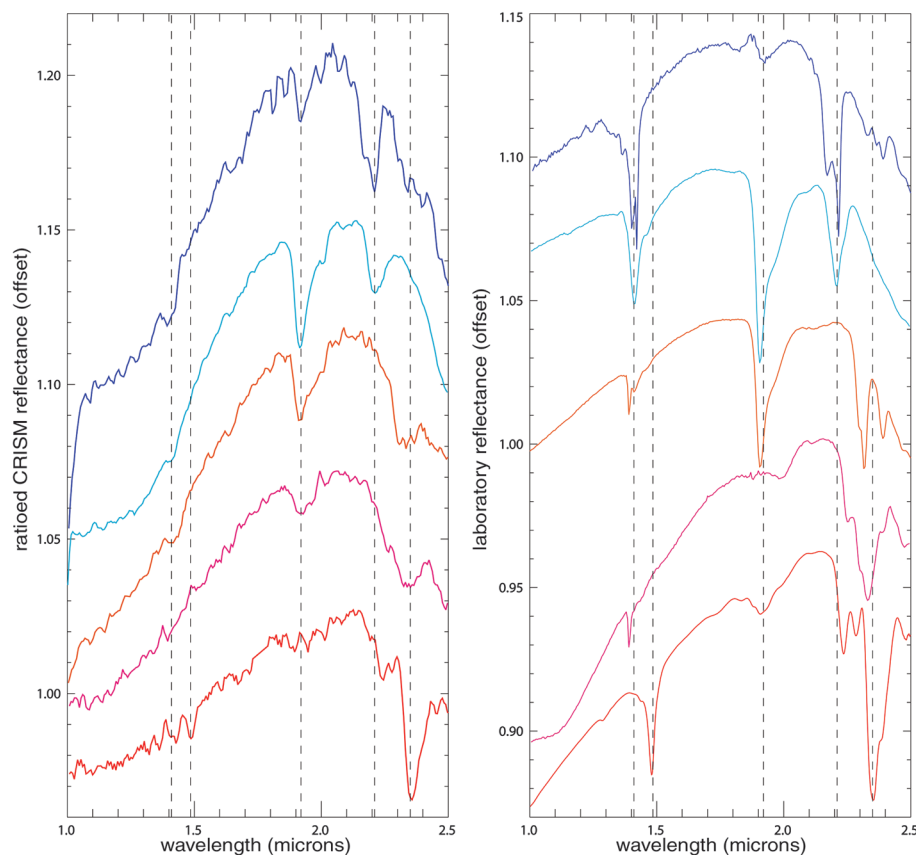


Fig. 2. CRISM hydrated silicate spectral signatures in northern plains craters (left). Candidate laboratory matches (right) are from the RELAB spectral database and (35). From top to bottom the colors are as follows: kaolinite, blue; montmorillonite, cyan; Fe/Mg saponite, orange; chlorite, purple; and prehnite, red. CRISM spectra are spatial averages of tens to hundreds of pixels.

formed by impact-driven hydrothermal alteration. Modeling shows that martian impact craters tens of km in size could have provided suitable pressure and temperature for phyllosilicate formation (29–31). Alteration would be strongest in the immediate vicinity of the central uplift and could have lasted 10^6 years. Recent calculations predict a variety of alteration minerals, for example, serpentine, chlorite, and the clay minerals nontronite and kaolinite (31). Some of these minerals are indeed identified; however, the min-

eral assemblage expected to be most abundant near the central uplift, a serpentine-hematite-talc assemblage, is not observed. The alteration minerals predicted in impact-induced hydrothermal systems vary in composition with the temperature, pressure, and water-to-rock ratio within the crater: One would therefore expect spatial gradients of abundances translating their stability. On the contrary, we observed unaltered olivine and phyllosilicates closely juxtaposed, randomly within the crater floors. The presence of prehnite

is also difficult to explain by an impact process. Lastly, if impact hydrothermalism was responsible for the formation of phyllosilicates, one would expect their presence in craters across a variety of units, but they were detected only when the impact penetrated the spectrally featureless Hesperian layer and exposed underlying Noachian rock with clear mafic mineral signatures.

The fourth scenario, supported by our observations, is that hydrated silicates in the northern plains craters formed by aqueous alteration

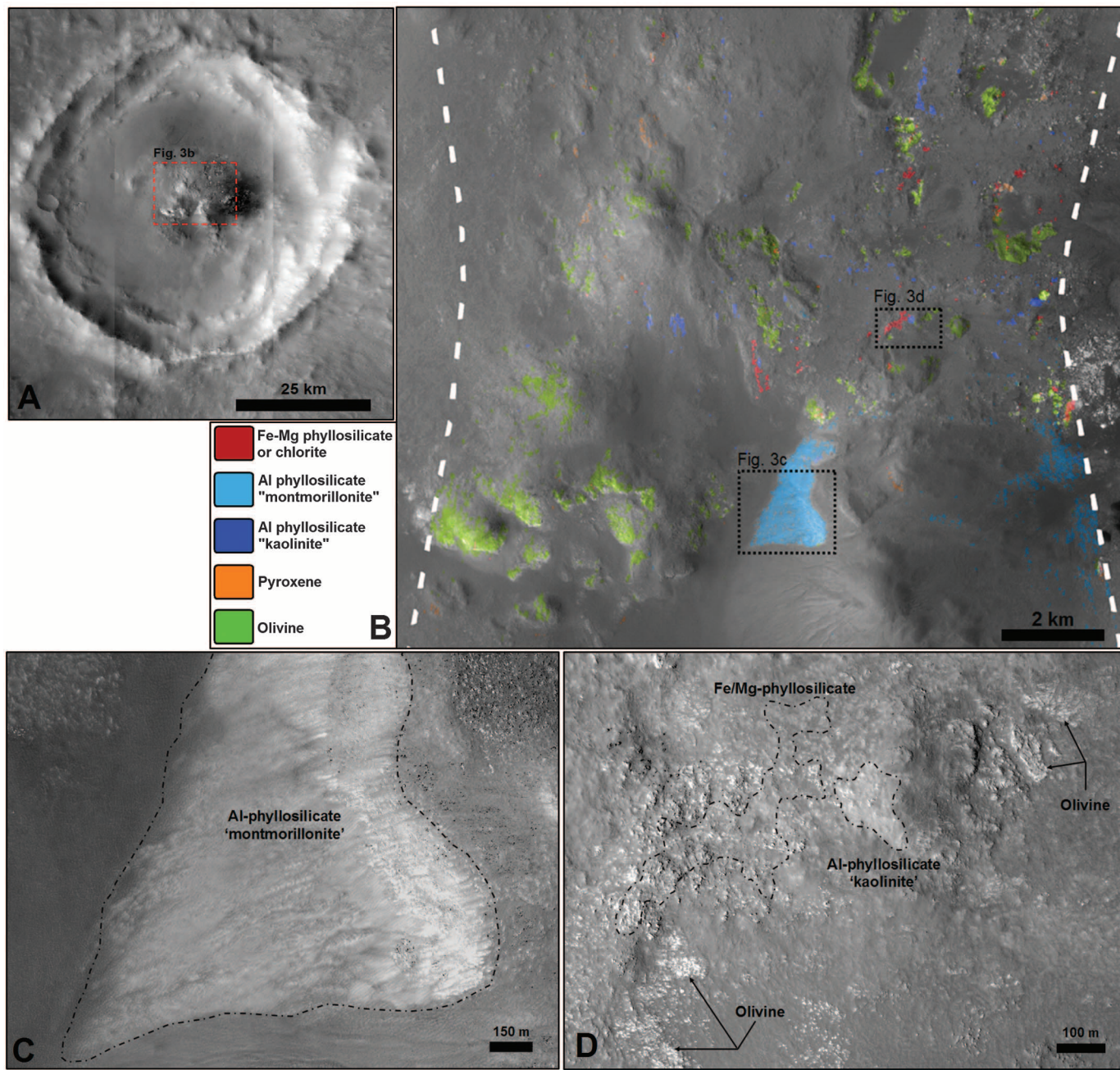


Fig. 3. (A) CTX–High-Resolution Stereo Camera (HRSC) mosaic of Stokes crater, centered at 171.35°E, 55.56°N. (B) CTX close-up (image P20_008686_2356). CRISM mineral maps from observation FRT0000ADA4 are overlain in color. The white dashed lines indicate the boundaries of the CRISM observation. (C) HiRISE close-up (image PSP_009332_2360) of the Al-

phyllosilicate “montmorillonite”-bearing unit. The sources of the material are the bright outcrops near the scarp summit (right), whereas the light-toned unit (left) is material transported down-slope. (D) HiRISE close-up (image PSP_009332_2360) showing outcrops of olivine, Fe/Mg-, and Al-phyllosilicates in close spatial association.

before emplacement of the Hesperian cover and then were excavated by impacts that penetrated the cover. On the basis of the estimated crater excavation depth (17), the craters in which hydrated minerals are detected are large enough to have reached the crust; the impacts have excavated material buried hundreds of meters to a km below surface, consistent with our observations of altered minerals both in central uplifts and rims and ejecta. The composition of the hydrated minerals also favors a formation predating the craters. Prehnite forms at high temperatures only attainable within the crust or hydrothermally within the central uplift of large (>30 km) craters (29, 30); it was detected in the central peak of a smaller crater as well as in the rim of Lyot crater, implicating formation at depth in the crust. More generally, the mineral assemblages found in these northern craters (such as smectites and chlorites) are very similar to those detected in craters in the southern highlands by using OMEGA and CRISM data

(6, 7, 32, 33). The geological contexts of highland detections point to formation by sustained aqueous alteration, commonly at elevated temperatures and possibly partly in the subsurface. Impact gardening, in particular during the likely late heavy bombardment, might have triggered some additional alteration of the mineral assemblages, but predominantly it might have mechanically mixed phyllosilicates and unaltered rock. In a similar way, craters that excavated hydrated minerals from beneath the northern plains may have induced some modifications of the mineral composition; however, the primary alteration took place within the crust, before excavation. The apparently random spatial distribution of unaltered olivine/pyroxene and phyllosilicate outcrops within the crater central structures is also consistent with the excavation of a differentiated and altered crust. Olivine is readily altered under aqueous conditions, which would be expected in an impact-generated hydrothermal environment.

Thus, the phyllosilicates detected in larger craters within the northern plains most likely record alteration processes that affected the northern crust before its being covered by kilometers-thick lava deposits. The similarities between their composition and those of the hydrated minerals in the southern highlands craters are an important indication that the martian crust was altered on a global scale during the Noachian period. This supports existence of an early environment conducive to the formation of life, with widespread liquid water, characterizing the phyllosian era (34).

This detection constrains the timing of ancient martian environments, in particular through the formation of the north-south hemispheric dichotomy; the heavy bombardment; and resurfacing of the northern lowlands by volcanism and sedimentary and volatile material. If the dichotomy formed by a giant impact, most of the record of preexisting shallow, low-temperature alteration would have been obliterated. Instead, craters

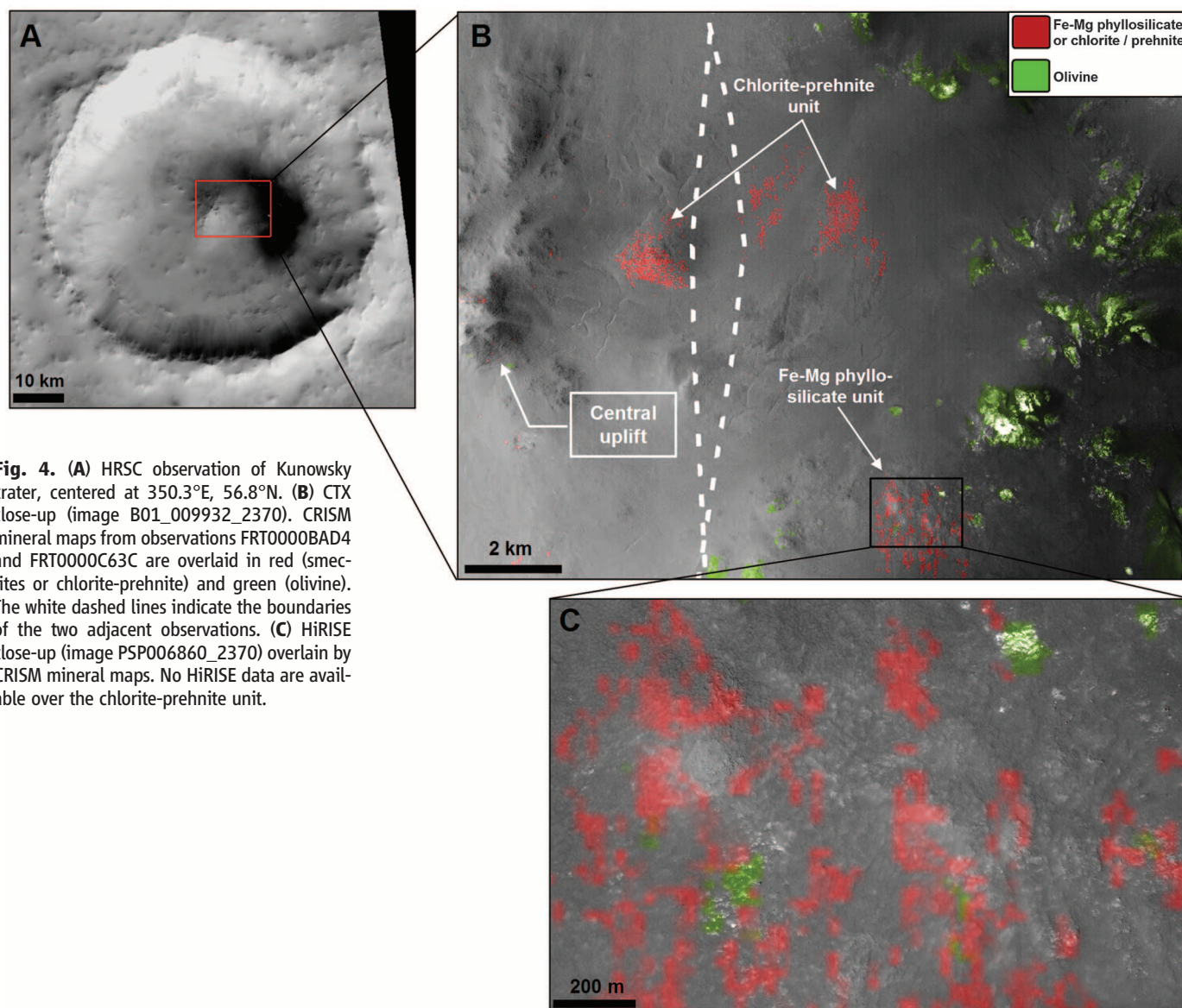


Fig. 4. (A) HRSC observation of Kunowsky crater, centered at 350.3°E, 56.8°N. (B) CTX close-up (image B01_009932_2370). CRISM mineral maps from observations FRT0000BAD4 and FRT0000C63C are overlaid in red (smectites or chlorite-prehnite) and green (olivine). The white dashed lines indicate the boundaries of the two adjacent observations. (C) HiRISE close-up (image PSP006860_2370) overlain by CRISM mineral maps. No HiRISE data are available over the chlorite-prehnite unit.

thousands of kilometers interior to the northern plains retain hydrated silicates. A likely sequence is thus as follows: The bulk of the aqueous alteration of the crust happened after the dichotomy formed but before the onset of volcanic activity that built the Tharsis plateau and contributed to the infilling of the northern plains. The phyllosian environment affected the entire planet during a highly restricted period of time.

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Supporting Online Material

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Figs. S1 and S2

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Hydrogen Isotopes Preclude Marine Hydrate CH₄ Emissions at the Onset of Dansgaard-Oeschger Events

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Thomas Blunier,³ Hubertus Fischer^{1,2}

The causes of past changes in the global methane cycle and especially the role of marine methane hydrate (clathrate) destabilization events are a matter of debate. Here we present evidence from the North Greenland Ice Core Project ice core based on the hydrogen isotopic composition of methane [$\delta D(CH_4)$] that clathrates did not cause atmospheric methane concentration to rise at the onset of Dansgaard-Oeschger (DO) events 7 and 8. Box modeling supports boreal wetland emissions as the most likely explanation for the interstadial increase. Moreover, our data show that $\delta D(CH_4)$ dropped 500 years before the onset of DO 8, with CH₄ concentration rising only slightly. This can be explained by an early climate response of boreal wetlands, which carry the strongly depleted isotopic signature of high-latitude precipitation at that time.

Rapid stadial-interstadial climate changes during Marine Isotope Stage 3 (MIS3), as recorded in Greenland ice (1), had a strong impact around the globe (2–5). Some of the stadials were accompanied by large discharges of icebergs from the Laurentide ice sheet, known as Heinrich events (4). Atmospheric methane concentrations in ice cores show

abrupt increases in concert with Dansgaard-Oeschger (DO) warmings (5, 6), although the causes of these methane jumps are not yet unambiguously understood. Preindustrial methane sources include wetlands, thermokarst lakes, ruminants, termites, biomass burning, ultraviolet radiation-induced release by plants, and clathrates (7–11). Wetlands, the major natural source of atmospheric methane, may be able to respond rapidly enough to changes in temperature and the hydrological cycle to account for the CH₄ increases (5, 7, 12, 13). Another hypothesis suggests that the observed rises were due to emissions of marine clathrates stored at the continental margins, which may have been destabilized by a warming of intermediate waters (14–16). Clathrate destabilization events were indeed found in selected marine sediments (14, 17), although their

contribution to the atmospheric budget has been questioned (5, 13, 18). A change in the CH₄ sink, and thus lifetime, may also have contributed to the observed CH₄ concentration changes.

Methanogenic pathways determine both the carbon and hydrogen isotopic signatures (8) of the emitted CH₄, which in turn can be used to better constrain the global methane budget (9). Source isotopic compositions may vary as a result of changes in methane precursor material, diffusion and oxidation processes that depend on water table depth in wetlands, or temperature changes in the aerobic zone of tundra soils (19). Moreover, the hydrogen isotopic composition of methane [$\delta D(CH_4)$] produced in terrestrial ecosystems is a function of the isotopic signature of precipitation (8). The hydrogen isotopic signature of precipitation changed globally because of the temporal variation in the isotopic composition of the ocean, which is a function of the size of polar ice sheets. Schrag *et al.* report δD values of the Last Glacial Maximum (LGM) ocean to be 6.5 to 9 per mil (‰) more enriched than those of today's ocean (20). Assuming a maximum sea-level rise of 30 m during DO 8 (21), this translates into a hydrogen isotopic shift of the well-mixed ocean of about 2‰. Superimposed on this global change, a stronger Rayleigh distillation effect in meteoric water is expected in high latitudes for cold climate conditions, due to the stronger pole-to-equator temperature gradient. For instance, water isotopes in modeled precipitation suggest that δD_{water} values were 15 to 30‰ lower in northern latitudes during the LGM, whereas values may have been 0 to 8‰ higher in the tropics (22).

Rapid changes in the low-latitude hydrological cycle are recorded in marine sediments (23), speleothems (3, 24), and leaf waxes in lake

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Detection of Hydrated Silicates in Crustal Outcrops in the Northern Plains of Mars

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Editor's Summary

Hydrated Minerals on Martian Northern Plains

The presence of hydrated minerals on the surface of Mars implies that the crust of the planet was once altered by the action of liquid water. This conclusion is well established for the ancient southern highlands of Mars, but the situation in the northern lowlands, which are thought to have been resurfaced by lava flows during the Hesperian period about 3 billion years ago, is not so clear. **Carter *et al.*** (p. 1682) report the detection of hydrated minerals in nine northern plain craters, which are thought to have exposed the ancient, pre-Hesperian crust. The results suggest that the degree of alteration of the ancient martian crust is more extensive than previously assumed.

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